

Spectrophotometric Determination of Formation Constants of Various Complexes of a Metal and Establishment of Probable Number of Such Successive Overlapping Complexes Using Kinetic Data

AKSHAYA K. INDRAYAN

*Department of Chemistry, Gurukula Kangri University
Hardwar-249 404, India*

Cerium(IV) forms a number of successive overlapping complexes with hypophosphorus acid. Yatsimirskii method is useful for the determination of formation constants of such complexes but fails to establish their probable number. A useful method is evolved by the application of an iterative method using kinetic data. Yatsimirskii method is applied by first assuming six complexes (1 : 1 to 1 : 6). Rate constants (k_1, k_2, k_3 etc.) are then calculated for each of them using kinetic rate equation. Values are found absurd. Whole of the procedure is then repeated by assuming four successive complexes leading to the values of formation constants (K_1, K_2, K_3 and K_4) for 1 : 1 to 1 : 4 complexes. The iterative method is then applied again for the determination of four rate constants. Very satisfactory values of k_1, k_2, k_3 , and k_4 conforming to the kinetic data, are obtained, indicating the probable number of complexes to be four and not six.

INTRODUCTION

Many of the metals are capable of forming more than one complex with the same ligand. When the number of such complexes is three or more (1 : 1, 1 : 2, 1 : 3, etc.) then sometimes it becomes very difficult to determine the formation constant of each and to assign the correct number of such successive overlapping complexes. In view of finding a solution to this problem, the present work was undertaken.

A new dimension was given to the spectrophotometric determination of formation constants of metal complexes by Ramette¹. For the determination of formation constant of a 1 : 1 complex, his method could be simplified to the following equation:

$$A + AK[L] = \epsilon_0[M]_T + \epsilon_1K[M]_T[L]$$

where A is observed absorbance of metal ligand mixture (taken at a suitable wavelength where ligand does not absorb), K the formation constant of 1 : 1 complex, $[L]$ the concentration of free ligand, ϵ_0 the extinction coefficient of metal and ϵ_1 the extinction coefficient of the complex. If the concentration of

ligand is taken in excess, free [L] may be assumed to be equal to the total [L]. Thus, by noting down the absorbance at three different ligand concentrations (all more than ten times metal) keeping the metal ion concentration $[M]_T$ to be constant, three different equations are obtained, leading to the determination of three unknown values, *i.e.*, ϵ_0 , ϵ_1 and K. The method not only gives the value of K for the complex, it gives the value of its extinction coefficient also. Since then various workers have used this method to determine the formation constants of metal complexes. Indrayan *et al.*^{2,3} determined the formation constants of $Ag^+ - H_3PO_2$ and $Ag^+ - H_3PO_3$ complexes² and of a silver(II) complex $Ag(ClO_4)_2$ in perchloric acid medium³ by this method.

In the case of formation of successive overlapping complexes Ramette's method creates difficulty. Another method, suggested by Newman and Hume⁴ seems to be quite complicated. It is only the Yatsimirskii method⁵ which seems to be quite useful in such cases, particularly when the number of successive overlapping complexes is more than two. In the present work this method has been applied as described by Beck⁶, however, with proper corrections. The present work deals, apart from determining the formation constants of various successive overlapping complexes, the determination of their probable number in the case of Ce(IV) and H_3PO_2 .

EXPERIMENTAL

A stock solution of Ce(IV) perchlorate was prepared by dissolving ceric ammonium nitrate (E. Merck) into water and adding ammonium hydroxide into it. Ceric hydroxide precipitate, so obtained, was allowed to settle for 48 hrs, the supernatant was decanted, precipitate was leached several times with water and finally dissolved in perchloric acid. The solution was filtered and standardised⁷ against ferrous ammonium sulphate using N-phenyl anthranilic acid as indicator.

Perchloric acid was Riedal AR grade 70 per cent and hypophosphorous acid was Riedal AR grade 32 per cent. Other chemicals employed were either AnalaR (B.D.H.) or GR (E. Merck). Corning glass vessels were employed for storing the solutions. Doubly distilled water was used for all solutions, the second distillation being from neutral potassium permanganate.

Optical measurements were made with a Beckmann UV spectrophotometer using 1 cm matching quartz cell. Absorbances of mixtures of cerium(IV) and hypophosphorous acid were measured at 285 nm and 30°C in 0.5 M perchloric acid at fixed concentration (8×10^{-5} M) of cerium(IV) and varying concentrations (2.5×10^{-3} to 5×10^{-3} M) of hypophosphorous acid. By using concentrations of cerium(IV) as low as permissible, the dimerisation in cerium(IV) was minimised without sacrificing accuracy in absorbance.

RESULTS AND DISCUSSION

The absorbances of Ce(IV)- H_3PO_2 mixture at varying concentrations of hypophosphorous acid are given in Table 1.

TABLE 1
 ABSORBANCE OF MIXTURES OF Ce(IV) AND
 H₃PO₂ AT DIFFERENT CONCENTRATIONS OF H₃PO₂
 [Ce(IV)] = 8 × 10⁻⁵ M; [HClO₄] = 0.5 M;
 temp. = 30°C; λ = 285 nm

10 ³ [H ₃ PO ₂] M	Absorbance
2.5	0.281
3.0	0.295
4.0	0.315
5.0	0.333

In the mixture, the total concentration of cerium(IV) is given by

$$[\text{Ce(IV)}]_{\text{T}} = [\text{Ce(IV)}]_{\text{f}} + \beta_1[\text{Ce(IV)}]_{\text{f}}[\text{H}_3\text{PO}_2]_{\text{f}} + \beta_2[\text{Ce(IV)}]_{\text{f}}[\text{H}_3\text{PO}_2]_{\text{f}}^2 + \beta_3[\text{Ce(IV)}]_{\text{f}}[\text{H}_3\text{PO}_2]_{\text{f}}^3 \quad (1)$$

where $\beta_1, \beta_2, \beta_3, \dots$ are gross formation constants of respectively 1 : 1; 1 : 1 and 1 : 2; 1 : 2, and 1 : 3, ... complexes.

The apparent absorbance A of the mixture is given by

$$A = \epsilon_0[\text{Ce(IV)}]_{\text{f}} + \epsilon_1\beta_1[\text{Ce(IV)}]_{\text{f}}[\text{H}_3\text{PO}_2]_{\text{f}} + \epsilon_2\beta_2[\text{Ce(IV)}]_{\text{f}}[\text{H}_3\text{PO}_2]_{\text{f}}^2 + \epsilon_3\beta_3[\text{Ce(IV)}]_{\text{f}}[\text{H}_3\text{PO}_2]_{\text{f}}^3 + \dots \quad (2)$$

where ϵ_0 is the extinction coefficient of free Ce(IV) and $\epsilon_1, \epsilon_2, \epsilon_3, \dots$ are the respective extinction coefficients of 1 : 1, 1 : 2, 1 : 3, ... complexes.

Equation (2) can be rewritten as

$$A = [\text{Ce(IV)}]_{\text{f}}(\epsilon_1\beta_1[\text{H}_3\text{PO}_2]_{\text{f}} + \epsilon_2\beta_2[\text{H}_3\text{PO}_2]_{\text{f}}^2 + \epsilon_3\beta_3[\text{H}_3\text{PO}_2]_{\text{f}}^3 + \dots) \quad (3)$$

Dividing equation (3) by equation (1)

$$\frac{A}{[\text{Ce(IV)}]_{\text{T}}} = \frac{\epsilon_0 + \epsilon_1\beta_1[\text{L}] + \epsilon_2\beta_2[\text{L}]^2 + \epsilon_3\beta_3[\text{L}]^3 + \dots}{1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2 + \beta_3[\text{L}]^3 + \dots} \quad (4)$$

where [L] denotes concentration of free ligand (H₃PO₂) which may, in fact, be taken equal to the concentration of total H₃PO₂ as the hypophosphorous acid is always in excess and its concentration undergoing complexation is small.

Cell thickness being 1 cm, A/[Ce(IV)]_T may be written as $\bar{\epsilon}$, i.e., apparent molar extinction coefficient.

Subtracting ϵ_0 from both sides in equation (4)

$$\Delta\bar{\epsilon} = \bar{\epsilon} - \epsilon_0 = \frac{(\epsilon_1 - \epsilon_0)\beta_1[\text{L}] + (\epsilon_2 - \epsilon_0)\beta_2[\text{L}]^2 + (\epsilon_3 - \epsilon_0)\beta_3[\text{L}]^3 + \dots}{1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2 + \beta_3[\text{L}]^3 + \dots} \quad (5)$$

$$\text{or } F = \frac{\bar{\epsilon} - \epsilon_0}{[\text{L}]} = \frac{\Delta\epsilon_1\beta_1 + \Delta\epsilon_2\beta_2[\text{L}] + \Delta\epsilon_3\beta_3[\text{L}]^2 + \dots}{1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2 + \beta_3[\text{L}]^3 + \dots} \quad (6)$$

Plotting F as a function of [L] and extrapolating to [L] = 0, we get

$$\lim_{[L] \rightarrow 0} F = F_1 = \Delta \epsilon_1 \beta_1 \quad (7)$$

Now,
$$F' = \frac{F - F_1}{[L]} = \frac{(\Delta \epsilon_2 \beta_2 - \Delta \epsilon_1 \beta_1^2) + (\Delta \epsilon_3 \beta_3 - \Delta \epsilon_1 \beta_1 \beta_2)[L] + \dots}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \dots} \quad (8)$$

Plotting F' as a function of [L] and extrapolating to [L] = 0, we get

$$\lim_{[L] \rightarrow 0} F' = F_2 = (\Delta \epsilon_2 \beta_2 - \Delta \epsilon_1 \beta_1^2)$$

or
$$F_2 = \Delta \epsilon_2 \beta_2 - F_1 \beta_1 \quad (9)$$

Proceeding in the same way, we get

$$F_3 = \Delta \epsilon_3 \beta_3 - F_1 \beta_2 - F_2 \beta_1 \quad (10)$$

Similarly F₄, F₅, F₆, etc. (depending upon the number of assumed complexes; values till F₆ are required if six successive complexes are assumed) can be determined. Now, dividing the numerator as well as denominator of equation (5) by [L]⁶ (assuming six complexes)⁸, we get

$$G = \Delta \bar{\epsilon} = \frac{\Delta \epsilon_1 \beta_1 [L]^{-5} + \Delta \epsilon_2 \beta_2 [L]^{-4} + \Delta \epsilon_3 \beta_3 [L]^{-3} + \dots}{[L]^{-6} + \beta_1 [L]^{-5} + \beta_2 [L]^{-4} + \beta_3 [L]^{-3} + \dots} \quad (11)$$

Plotting G as a function of [L]⁻¹ and extrapolating to [L]⁻¹ = 0, we get

$$\lim_{[L]^{-1} \rightarrow 0} G = G_1 = \Delta \epsilon_6 \beta_6 / \beta_6 = \Delta \epsilon_6 \quad (12)$$

Now

$$G' = \frac{G - G_1}{[L]^{-1}} = \frac{(\Delta \epsilon_5 \beta_5 - \Delta \epsilon_6 \beta_5) + (\Delta \epsilon_4 \beta_4 - \Delta \epsilon_6 \beta_4)[L]^{-1} + (\Delta \epsilon_3 \beta_3 - \Delta \epsilon_6 \beta_3)[L]^{-2} + \dots}{\beta_6 + \beta_5 [L]^{-1} + \beta_4 [L]^{-2} + \beta_3 [L]^{-3} + \dots} \quad (13)$$

Plotting G' as a function of [L]⁻¹ and extrapolating to [L]⁻¹ = 0, we get

$$\lim_{[L]^{-1} \rightarrow 0} G' = G_2 = (\Delta \epsilon_5 \beta_5 - \Delta \epsilon_6 \beta_5) / \beta_6$$

or
$$G_2 = (\Delta \epsilon_5 \beta_5 - G_1 \beta_5) / \beta_6 \quad (14)$$

Proceeding in the same way, we get

$$G_3 = (\Delta \epsilon_4 \beta_4 - G_1 \beta_4 - G_2 \beta_5) / \beta_6 \quad (15)$$

Similarly G₄, G₅ and G₆ can be calculated.

Table 2 gives the values of F₁ to F₆ and G₁ to G₆ obtained for the present work. Solving equations (7), (9), (10) and (12), (14), (15) simultaneously, the values of β₁, β₂, β₃, β₄, β₅ and β₆ could be determined in terms of F₁, F₂, F₃, . . . , G₁,

G_2, G_3, \dots Latter quantities being known, the values of $\beta_1, \beta_2, \beta_3$ etc. could be known and thus K_1, K_2, K_3 etc. In the present work, the values of formation constants of 1 : 1, 1 : 2, 1 : 3, 1 : 4, 1 : 5 and 1 : 6 successive complexes were obtained to be 1.17×10^3 (K_1), 5.606×10^2 (K_2), 3.55×10^2 (K_3), 2.422×10^2 (K_4), 1.539×10^2 (K_5) and 0.46×10^2 (K_6) respectively.

TABLE 2
VALUES OF F_1 TO F_6 AND G_1 TO G_6

F_1	14.0×10^5	G_1	3.2×10^3
F_2	-3.0×10^8	G	-2.9
F_3	2.9×10^{10}	G_3	-0.45×10^{-3}
F_4	-13.0×10^{11}	G_4	0.70×10^{-6}
F_5	13.0×10^{14}	G_5	-0.01×10^{-9}
F_6	5.0×10^{15}	G_6	-0.05×10^{-12}

Note Powers raised to ten are the ones directly obtained in calculations. To give a convenient picture, they are not being converted to uniformity.

Above calculations have been made by preassumption. Formation of six successive complexes has been presumed. But how to be sure of the formation of such a number of complexes? To ascertain the probable number of complexes seems to be a problem, whether they are three, four or six. Yatsimirskii method does not give an answer to this. An iterative method using the kinetic data gives a somewhat satisfactory answer to this if the rate law is known. In the present work, application of iterative method indicated that probable number of successive overlapping complexes between cerium(IV) and hypophosphorous acid is *four* and not six. In the case under investigation, Ce(IV)- H_3PO_2 complexes, the rates for Ag(I) catalysed oxidation of hypophosphorous acid with cerium(IV)⁹ were determined. Rate constants were then calculated on the basis of the complexes mentioned above by applying the iterative method in the following manner:

The rate law for above reaction was found to be⁹

$$\text{Rate} = \frac{-d[\text{Ce(IV)}]}{dt} = \text{Uncatalysed rate} + [\text{Ce(IV)}]_f [\text{H}_3\text{PO}_2]_f^2 [\text{Ag(I)}][\text{H}^+] \times (k_1\beta_1 + k_2\beta_2[\text{H}_3\text{PO}_2]_f + k_3\beta_3[\text{H}_3\text{PO}_2]_f^2 + \dots) \quad (16)$$

where k_1, k_2, k_3, \dots are rate constants for respectively 1 : 1, 1 : 2, 1 : 3, \dots complexes.

The concentrations of free Ce(IV) and free H_3PO_2 were calculated by successive approximations from the equilibrium and mass balance relations, *i.e.*, total concentration of Ce(IV) is given by

$$[\text{Ce(IV)}]_T = [\text{Ce(IV)}]_f + K_1[\text{Ce(IV)}]_f[\text{H}_3\text{PO}_2]_f + K_1K_2[\text{Ce(IV)}]_f[\text{H}_3\text{PO}_2]_f^2 + K_1K_2K_3[\text{Ce(IV)}]_f[\text{H}_3\text{PO}_2]_f^3 + \dots$$

and total concentration of H_3PO_2 is given by

$$[\text{H}_3\text{PO}_2]_{\text{T}} = [\text{H}_3\text{PO}_2]_{\text{f}} + K_1[\text{Ce(IV)}]_{\text{f}}[\text{H}_3\text{PO}_2]_{\text{f}} + 2K_1K_2[\text{Ce(IV)}]_{\text{f}}[\text{H}_3\text{PO}_2]_{\text{f}}^2 \\ + 3K_1K_2K_3[\text{Ce(IV)}]_{\text{f}}[\text{H}_3\text{PO}_2]_{\text{f}}^3 + \dots$$

Obtaining the values of $[\text{Ce(IV)}]_{\text{f}}$ and $[\text{H}_3\text{PO}_2]_{\text{f}}$ for different reactant concentrations, the rate constants k_1 , k_2 , k_3 etc. could then be calculated in the following manner:

From equation (16) we have

$$\frac{\text{Total rate} - \text{uncatalysed rate}}{[\text{Ce(IV)}]_{\text{f}}[\text{Ag(I)}][\text{H}^+][\text{H}_3\text{PO}_2]_{\text{f}}^2} = k_1\beta_1 + k_2\beta_2[\text{H}_3\text{PO}_2]_{\text{f}} + k_3\beta_3[\text{H}_3\text{PO}_2]_{\text{f}}^2 \\ + k_4\beta_4[\text{H}_3\text{PO}_2]_{\text{f}}^3 + \dots$$

or
$$x_1 = k_1\beta_1 + k_2\beta_2[\text{H}_3\text{PO}_2]_{\text{f}} + k_3\beta_3[\text{H}_3\text{PO}_2]_{\text{f}}^2 + \dots$$

Table 3 shows the values of $[\text{Ce(IV)}]_{\text{f}}$ and $[\text{H}_3\text{PO}_2]_{\text{f}}$ obtained by mass balance equations and also the rates of catalysed and uncatalysed reactions obtained by kinetic studies at different concentrations of total H_3PO_2 . A graph plotted between x_1 and $[\text{H}_3\text{PO}_2]_{\text{f}}$ gives a curve. Its extrapolation to zero gives the values of $k_1\beta_1$. β_1 being known (1.17×10^3), the value of k_1 could be calculated.

TABLE 3
VALUES OF FREE $[\text{Ce(IV)}]$ AND FREE $[\text{H}_3\text{PO}_2]$ AT DIFFERENT TOTAL $[\text{Ce(IV)}]$
AND TOTAL $[\text{H}_3\text{PO}_2]$ AND THE CORRESPONDING REACTION RATES
(ASSUMING SIX COMPLEXES)
[HClO_4] = 0.5 M; temp. = 30°C

10^3 [Ce(IV)] Total M	10^3 [H ₃ PO ₂] Total M	10^3 [Ce(IV)] Free M	10^3 [H ₃ PO ₂] Free M	10^7 (Rate of uncatalysed reaction) M/sec	10^7 (Rate of catalysed† reaction) M/sec
1.0	3.0	0.1937	1.474	1.5	3.53
1.0	4.0	0.1121	1.990	2.0	5.20
1.0	5.0	0.0642	2.553	2.5	6.80
1.0	6.0	0.0363	3.169	3.0	8.50

†For catalysed reactions, the catalyst $[\text{Ag(I)}] = 5 \times 10^{-5}$ M

Now, we have

$$\frac{x_1 - k_1\beta_1}{[\text{H}_3\text{PO}_2]_{\text{f}}} = k_2\beta_2 + k_3\beta_3[\text{H}_3\text{PO}_2]_{\text{f}} + k_4\beta_4[\text{H}_3\text{PO}_2]_{\text{f}}^2 + \dots$$

or
$$x_2 = k_2\beta_2 + k_3\beta_3[\text{H}_3\text{PO}_2]_{\text{f}} + k_4\beta_4[\text{H}_3\text{PO}_2]_{\text{f}}^2 + \dots$$

Plotting x_2 against $[\text{H}_3\text{PO}_2]_{\text{f}}$ and extrapolating to zero, the value of $k_2\beta_2$ is obtained and, thus, k_2 is calculated. Proceeding in the same way the determination of k_3 and k_4 etc. was tried. Values of k_1 and k_2 were satisfactorily found to be $(4.27 \pm 0.2) \times 10^3$ and $(0.915 \pm 0.05) \times 10^4 \text{ M}^2 \text{ S}^{-1}$ respectively. But, the graph

plotted for k_3 is not a satisfactory one. However, k_3 calculated to the best was found to be $(0.644 \pm 0.06) \times 10^4 \text{ M}^2 \text{ S}^{-1}$. Proceeding for k_4 , the plot was found to be very much absurd and the value of k_4 and onwards could not be determined. The iterative method applied so far seems to be mathematically true and applicable. So, its failure here leads to the idea that the actual complexes may not be six. Whole of the method was then applied by assuming four complexes. The processing yielded the values of formation constants of the four complexes (1:1, 1:2, 1:3 and 1:4) to be 3.65×10^3 (K_1), 2.15×10^3 (K_2), 1.50×10^3 (K_3), and 9.5×10^2 (K_4) M^{-1} respectively (all values with a precision of ± 10 –15 per cent). Using these values the concentrations of free H_3PO_2 and free Ce(IV) were calculated for same concentrations of reactants. Table 4 gives these concentrations along with the rates of catalysed and uncatalysed reactions determined by kinetic studies. Proceeding with these values the iterative method was applied again for the determination of rate constants. Quite satisfactory plots in graph were obtained and values of k_1 , k_2 , k_3 and k_4 were found to be respectively $(5.4 \pm 0.3) \times 10^3$, $(1.65 \pm 0.2) \times 10^4$, $(2.05 \pm 0.2) \times 10^4$ and $(2.5 \pm 0.3) \times 10^3 \text{ M}^2 \text{ S}^{-1}$. Thus, only four complexes, i.e., 1:1, 1:2, 1:3 and 1:4 are indicated between Ce(IV) and H_3PO_2 . 1:5 and 1:6 complexes are irrelevant or they are kinetically inactive.

TABLE 4
VALUES OF FREE $[\text{Ce(IV)}]$ AND FREE $[\text{H}_3\text{PO}_2]$ AT DIFFERENT TOTAL $[\text{Ce(IV)}]$
AND TOTAL $[\text{H}_3\text{PO}_2]$ AND THE CORRESPONDING REACTION RATES (ASSUM-
ING FOUR COMPLEXES)
 $[\text{HClO}_4] = 0.5 \text{ M}$; temp. = 30°C

$10^3 [\text{Ce(IV)}]$ Total M	$10^3 [\text{H}_3\text{PO}_2]$ Total M	$10^3 [\text{Ce(IV)}]$ Free M	$10^3 [\text{H}_3\text{PO}_2]$ Free M	10^7 (Rate of uncatalysed reaction) M/sec	10^7 (Rate of catalysed† reaction) M/sec
1.0	3.0	0.0744	0.6863	1.5	3.53
1.0	4.0	0.02185	1.0951	2.0	5.20
1.0	5.0	0.00558	1.6964	2.5	6.80
1.0	6.0	0.001547	2.4674	3.0	8.50

†For catalysed reactions, the catalyst $[\text{Ag(I)}] = 5 \times 10^{-5} \text{ M}$

ACKNOWLEDGEMENT

The author is thankful to Prof. Y.K. Gupta (University of Rajasthan, Jaipur) for his guidance throughout the work and to Veena Indrayan for her help in undertaking the marathon calculations.

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(Received: 8 July 1992; Accepted: 8 March 1993)

AJC-597